A Neutron Scattering Study of Water

and Ionic Solutions

By G. J. Safford, P. S. Leung, Union Carbide Corporation, Tuxedo, New York, for Office of Saline Water, C. M. Wong, Director; W. Sherman Gillam, Assistant Director, Research; W. H. McCoy, Chief, Chemical Physics Division.

Contract No. 14–01–0001–1484

UNITED STATES DEPARTMENT OF THE INTERIOR   •   Walter J. Hickel, Secretary
Carl L. Klein, Assistant Secretary for Water Quality and Research

As the Nation's principal conservation agency, the Department of the Interior has basic responsibilities for water, fish, wildlife, mineral, land, park, and recreational resources. Indian Territorial affairs are other major concerns of America's "Department of Natural Resources".

The Department works to assure the wisest choice in managing all our resources so each will make its full contribution to a better United States—now and in the future.

FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

SUMMARY

The dependences on concentration, on cation, and on anion of
the intermolecular frequencies and the diffusive kinetics of H_2O molecules
in aqueous solutions have been investigated by neutron inelastic scatter-
ing. Most measurements were at $1°C$ where the diffusive kinetics are in
accord with a delayed-diffusion mechanism and values of the self-diffusion
coefficients and residence times can be obtained. At lower concentrations
(≤ 0.5 m) where the spectra primarily reflect the solvent structure, solu-
tions of $MgCl_2$, NaCl, and CsCl show intermolecular frequencies and values
of D and τ_0 nearly identical to water. Water frequencies persist to above
4.6 m in KCl solutions, but for LiCl any correspondence to water is lost
between 0.05 m and 0.2 m. With increasing concentration, the correspon-
dence to water is lost and new frequencies characteristic of primary ion-
water hydration complexes appear and intensify; the D's decrease and the
τ_0's increase relative to water for KF, NaCl, LiCl and $MgCl_2$ ("positive
hydration"); and the reverse is true for CsCl, CsBr, KSCN, KI, KBr and
KCl ("negative hydration"). With increasing CsCl concentration the D's
increase and the τ_0's decrease initially, but "saturate" and are nearly
constant above 4.6 m, possibly due to increased ion-pairing. At higher
concentrations of KSCN the values of D and τ_0 go through a maximum and
minimum respectively, and approach the values for water in correspondence
with a decrease in the "negative hydration" of this salt at high concen-

trations. This behavior indicates that while the SCN^- may increase the average diffusive mobility in the solvent relative to water, reorientations of H_2O molecules in primary hydration coordinations are at least as restricted as those in water. In solutions that contain small- and/or highly-charged cations (i.e., Li^+, La^{+3}) the frequencies and diffusive parameters are primarily determined by the cation and only secondarily affected by monovalent anions. Thus, replacement of Cl^- ions by an equivalent concentration of NO_3^- ion causes small broadenings of the intermolecular frequencies together with a small increase in D and decrease in τ_o, corresponding to a weak "structure-breaking" effect. In contrast, the intermolecular frequencies and the diffusive kinetics show a strong dependence on anion for solutions of larger, singly-charged cations. Thus, in solutions of potassium salts the "structure-breaking" influence of the halide anion increases as $Cl^- < Br^- < I^-$, and F^- acts as a "structure-maker." The larger structure-breaking influence of the Br^- ion relative to the Cl^- ion is less pronounced in concentrated cesium ion solutions, as stronger ion-pairing in CsCl reduces the relative number of primary cation-water coordinations. Experimental evidence and a tentative explanation are given for a rapid variation with temperature of the intermolecular frequencies and the diffusive parameters in a 4.6 m KCl solution near 25°C.

I. INTRODUCTION

The results of a neutron inelastic scattering (NIS) investigation of the influence of ionic solutes on the intermolecular vibrations and the diffusive kinetics of the solvent molecules in concentrated aqueous solutions has been reported previously[1]. The details of the NIS technique, the associated theories, and their applications to the studies of the motions of H_2O molecules in liquids and solids have been extensively described in the literature[2][3][4]. As a result of the large scattering cross section of hydrogen relative to other elements, the spectra reflect the vibrational and diffusive motions of the H_2O molecules in solutions. NIS spectra are not subject to optical selection rules and, hence, all intermolecular vibrations below 900 cm^{-1} and diffusive motions that occur within the interaction time[5] can, in principle, be observed. The previous NIS measurements have shown that:

(a) In the inelastic spectra of concentrated aqueous solutions containing strongly hydrating small- and/or highly-charged ions (e.g., La^{+3}, Mg^{+2}, Li^{+1} and F^{-1}) intermolecular frequencies are observed that closely correspond to the rocking, twisting and wagging librational modes, and to ion-water stretching and bending modes in the NIS spectra of the corresponding solid salt hydrates. This similarity suggested that the thermolabile local orderings in the primary hydration layers of such ions in solution were similar to those of their respective solid hydrates. The strong-primary ion-water interactions (which could, in certain cases, be partially covalent[6]) disrupt the initial solvent structure and give rise to these specific ion-water hydration coordinations. Increasing the temperature partially disorders these coordinations and increases the anharmonicity and multiphonon contributions thus causing the corresponding frequencies to broaden and become less resolved.

(b) Concentrated solutions of the larger, singly-charged cations (e.g., Cs^+, K^+ and Na^+) also showed intermolecular frequencies specific to a given salt and characteristic of primary ion-water complexes which

1

while weaker than the primary ion-water coordinations of small- or highly-charged cations, were stronger than the average H_2O-H_2O bond in pure water. Thus, with increasing temperature, remnant H_2O-H_2O coordinations were more rapidly disrupted than the primary ion-water coordinations. The relative number of primary hydration waters increased, and the corresponding intermolecular frequencies became sharper and better defined.

(c) From the analysis of the angular and temperature dependences of the width of the diffusively broadened incident line (the "quasi-elastic component"), it was determined that below 25°C a delayed diffusion model[7] adequately approximated the diffusive kinetics. Within experimental uncertainty, values of self-diffusion coefficients (D) and of residence times (τ_O) were obtained in reasonable agreement with those from other techniques. In general, for solutions containing small- and/or highly-charged ions at all temperatures, the D's were decreased and the τ's were increased relative to water. Thus, in the terminology of Samoilov,[8] such ions acted as "positive hydrators." In contrast, at lower temperatures in solutions of larger, singly-charged ions (even though ion-water complexes were formed) the D's were increased and τ_O's decreased relative to water indicating an increased reorientational mobility for H_2O molecules in primary layers and/or in regions more distant from the ions. These ions then acted as "negative hydrators." For certain salts of these solutions (e.g., KCl and CsCl) increasing temperature caused the values of the D's and the τ_O's to closely approach those for water in correspondence with a decrease in the "negative hydration" or in the relative "structure-breaking" properties of such salts.

In the present investigation, further measurements have been made to study both intermolecular frequencies and the diffusive kinetics as a function of solute concentration, including more dilute solutions than previously investigated. Typically, concentrations between 0.5 m and the saturation limit of a given salt were studied. At 0.5 m (approximately equal to 110 H_2O's per ion pair) the spectral contributions of the relatively small number of H_2O molecules in primary hydration layers are negligible and the spectra are characteristic of the "bulk-solvent." The

degree to which the structure of pure water can persist in dilute solutions and the relative influences of ionic size, charge, and the strength and coordinations in the primary layers in disrupting the more remote bulk solvent have been the subject of considerable interest. Thus, Frank and Wen[9] argued for a region of disrupted water structure intermediate to the primary hydration layer and the distant solvent. Further, Samoilov[8] has emphasized the tendency of ions to hydrate in dilute solutions so that the minimum modification of the solvent structure occurs. In such an "intermediate region" the average number of bonds per H_2O would be expected in general to be lower than for water and the reorientational freedom of H_2O molecules expected to increase. However, it has also been argued[10] that strong primary ion-water interactions can lead to a cooperative strengthening of the bonding between H_2O molecules beyond the primary layer, which could decrease their reorientational freedom.

In addition, in the present experiments the influence of different anions on the intermolecular vibrational frequencies and the diffusive dynamics has been further investigated in more concentrated solutions. For solutions of strongly hydrating La^{+3} and Li^{+1} cations, the relative influence of Cl^- vs. NO_3^- anions were studied. For solutions of cations of large charge-to-radius (K^+ and Cs^+) variations in inelastic and quasi-elastic components were compared for KCl, KBr, KI and KSCN and for CsCl and CsBr. In order to simplify the interpretation of the data, all the above measurements were made at 1°C where the simple delayed diffusion mechanism has been shown[1] to be most valid.

II. EXPERIMENTAL

A. Instrumental

The present measurements were made using a beryllium filtered incident beam and a neutron time-of-flight spectrometer (Figure 1) which has been described previously.[11] General descriptions of this type of spectrometer and its applications to studies of liquids are in the literature[12]. The samples of the solutions (prepared from analytical-grade reagents and deionized water) were contained in grooves of average thickness

of 0.42 mm in an Al plate backed by a flat piece of cadmium. A 2μ layer
of an inert polymer film protected against corrosion, and the cell was
shielded with cadmium to prevent scattering by the sample holder. As
reported previously[1], the polymer film and the Al window gave negli-
gible spectral distortions or background contributions and the sample
thickness used[1] gave negligible spectral contributions due to multiple
scattering. For the spectra taken at 274°K, the sample was cooled by
circulating water from an ice-water bath, appropriately shielded to avoid the
scattering of neutrons by the coolant.

B. Analysis of Data

The procedures used for the treatment of the data, for checking
its reliability and reproducibility, and for the analysis of the quasi-
elastic components have been extensively described in previous papers[1][13].
Hence, only a summary will be given here.

The observed spectra were corrected for background, counter
efficiency, and chopper transmission. The background corrections were
made by a channel-by-channel subtraction of spectra obtained for the empty
sample holder. The background was predominantly a flat component upon
which was superimposed a weaker, broad distribution centering at about
channel 146. The latter component varied with rotor speed as expected
for the "180° burst." Small but significant variations occurred in the
background with scattering angle and cell geometry, but spectra independent
of a given cell could be systematically obtained after background correc-
tions. Typical statistical uncertainties are shown with the reported spectra
and correspond to plus or minus one standard deviation as calculated from
the total number of counts and from the number of background counts per
channel. The solid curves in the neutron spectra were averaged through the
data points with regard to the statistical uncertainties. Where a
singularity was marginal in intensity with regard to statistical error, it
was assigned only if it was systematically reproduced at more than one
scattering angle, temperature, and concentration. In addition to

statistical considerations, the reproducibility and reliability of spectral features were tested by (a) comparisons of spectra re-measured with fresh solutions, (b) comparisons of spectra for different scattering angles and for different temperatures, (c) comparisons of data collected on the four independent counter banks, electronics, and memory banks of the time-of-flight analyzer, and (d) comparisons with background spectra for the empty cell to show that no spectral features arose from neutrons scattered by the sample holder or shielding.

In the analysis to obtain the width, Γ (the Lorentz half-width at half-maximum), of the quasi-elastic distribution, the low frequency inelastic contribution was estimated and subtracted from the observed spectra using a gas model of mass 18[14][15]. A value of Γ was then chosen to yield the optimum agreement in shape between the measured incident distribution, broadened by Lorentzian functions[7] of varying half-widths at half-maximum, Γ, and an observed quasi-elastic maximum. The errors shown represent the limits to which Γ could be varied without incurring variations in shape outside the accuracy of the data.

The measurements for most of the spectra were made at $274°K$ where the delayed-diffusion limit of the general Singwi-Sjolander model[7] would be most valid. For this model

$$\Gamma = \frac{\hbar}{\tau_0}\left(1 - \frac{e^{-2W}}{1+K^2 D\tau_0}\right) \tag{1}$$

where

$$K^2 = k_0{}^2 + k_f{}^2 - 2\,k_0 k_f \cos\phi$$
and for $k_0 \approx k_f$

$$\left|\overrightarrow{K^2}\right| \approx 4\,k_0{}^2 \sin^2 \phi/2,$$

$\overrightarrow{k_0}$ = initial neutron momentum vector

$\overrightarrow{k_f}$ = final neutron momentum vector

ϕ = scattering angle

τ_0 = "residence time"

D = self-diffusion coefficient

e^{-2W} = the Debye-Waller factor

Values of D and τ_0 were chosen to yield the optimum fit to Γ vs. K^2.

5

III. RESULTS

The NIS spectra reflect the vibrational and diffusive motions of H_2O molecules characteristic of the "bulk-solvent" for dilute solutions and of primary ion-water complexes in concentrated solutions. At lower concentrations (typically of 0.5 m and below which correspond to more than 110 H_2O's per ion-pair) the spectra for the CsCl, NaCl, and $MgCl_2$ solutions show intermolecular modes at frequencies which are in pronounced correspondence with those observed for water (Figure 2). However, such a correspondence is not observed for dilute LiCl solutions until a lower concentration (about 0.05 m) is reached and, in KCl solutions, frequencies characteristic of water persist even to concentrations as high as 4.6 m. In the spectra of these solutions, frequency shifts relative to water within the experimental resolution cannot be precluded, and variations in the relative intensities of the maxima do occur. Nevertheless, the frequencies for torsional components[1] as well as the lower frequency modes, show a degree of correspondence with those for water, which is lost with increasing concentration in a manner specific to a given salt.

The curves of Γ vs. K^2 for such dilute solutions are nearly within experimental error of that for water (Figure 2), implying a similarity in the values of both the self-diffusion coefficients and the residence times. Any changes in the activation energy must be small compared to that for the energy of a hydrogen bond in water (approximately 2.5 kcal/mole[1]). While the individual points in the Γ vs. K^2 curves are within error of those for water, the points for CsCl lie uniformly above that for water while those for $MgCl_2$ and LiCl lie systematically below.

Thus, despite the different hydrating powers of the magnesium, sodium and cesium ions, it appears that at concentrations below about 0.5 m, the structure of the solvent is not strongly disrupted relative to water. In contrast, LiCl is more effective in disrupting

the solvent structure than the above salts while KCl is less effective.

The ability of cations to disrupt the structure of water can depend not only upon the strength (relative to water) of their primary ion-water coordinations but also upon the degree of structural dissimilarity between the H_2O molecules ordered in primary hydration layers and the solvent structure distant from the ions.[10] In general, in an "intermediate region" about the hydrated ions, the average number of bonds per H_2O would be reduced relative to water due to the "structural mismatch" and resulting strains. The size and relative number of H_2O molecules in the intermediate region as well as their diffusive freedom would depend upon the transition from the region where the structure and forces are determined by bulk water structure, to the region where they are determined by primary ion-water coordinations.

The apparent ability of the Li^+ ion, relative to Na^+, Mg^+ and Cs^+ ions, to strain and disrupt the solvent structure at lower concentrations could in part be a result of the small number of strongly coordinated and specifically oriented primary water molecules. The small Li^+ ions form a strongly coordinated primary hydration layer and possibly even a second layer[16]. The primary layer has been reported[17] to involve four H_2O's in a tetrahedral coordination. In contrast, larger ions like Na^+, Mg^{+2}, and Cs^+ can accommodate a larger number of primary H_2O's. Thus, the H_2O molecules adjacent to the hydrated Li^+ ions might have to undergo sufficiently large reorientations to bond to the hydration layer waters so that a cooperative structural readjustment, involving many molecules, would result. In contrast, larger ions having a greater number of primary waters would not require as large a reorientation from the water structure to couple to the primary hydration H_2O's about an ion.

With increasing concentration (Figures 4 through 6) the correspondence with water frequencies characteristic of lower concentrations is lost and, as reported previously[1], frequencies characteristic of librational and metal oxygen stretching and bending modes in the ion-water complexes are observed. The broadening and damping of the inelastic

spectra at 2.5 m CsCl, at 4.6 m in NaCl, and at 4.6 m in MgCl$_2$, undoubtedly reflect contributions of both frequencies characteristic of the disrupted solvent and frequencies characteristic of primary ion-water complexes. The latter frequencies grow and become more pronounced as the concentration increases. For small- or highly-charged ions such frequencies have been attributed to cation-water hydration complexes with a short-range ordering similar to the corresponding solid hydrates. They may involve a degree of covalency in the primary cation-water interaction[6].

In Figure 7 the inelastic spectra of La(NO$_3$)$_3$ and LaCl$_3$ are intercompared as are those for LiCl, LiSCN, and LiNO$_3$. While both the LaCl$_3$ and La(NO$_3$)$_3$ spectra show large departures from water, a strong correspondence is observed between their intermolecular frequencies. A similar but less pronounced correspondence involving larger variations in the relative sharpness of maxima between the spectra of the three lithium salts is also observed. These results emphasize that the ordering of the H$_2$O molecules in the primary hydration layers in these solutions arises from the strong coordinations of the primary water molecules with small and/or highly charged cations and is only secondarily influenced by these -1 anions. In correspondence, the observed variations with anions of the associated diffusive kinetics and parameters are smaller than those observed with cations (Figure 8). The Γ vs. K^2 curve for La(NO$_3$)$_3$, lies close to but systematically below that for LaCl$_3$ and the inelastic spectrum is also slightly broader for La(NO$_3$)$_3$. These results suggest that NO$_3^-$ ions, relative to the Cl$^-$ ions, may partially "loosen" and perturb the ordering of solvent molecules about the cations, and hence the structure-breaking effect (negative hydration) for nitrate ion is larger than that for chloride ion. In contrast to the La^{+3} and Li$^+$ salts, no similar correspondence is observed at 1°C between the intermolecular frequencies for the four potassium salts shown in Figure 9. The diffusive kinetics also show a larger anion dependence (Figure 8). Thus, the destructive effect of an anion appears to increase with the radius of the cation.

A number of features of the influence of anions, of concentration, and of temperature will now be considered in more detail for cesium and potassium salts. At lower temperatures ($1°C$) the inelastic spectra of CsCl and CsBr solutions of concentrations typically above 2 m show frequencies differing from those for water and characteristic of ion-water complexes. While variations occur in their intensities, these inelastic maxima for CsCl above 4.6 m and CsBr above 2.5 m occur at nearly the same frequencies and are not strongly anion dependent. The similarity in the frequencies suggests that they are primarily associated with cation-water coordinations. Simultaneously, the curves of Γ vs. K^2 for CsBr and CsCl lie above that for KBr and KCl, corresponding to a relatively stronger "structure-breaking" effect and to an increase in D and decrease in τ_O. Thus, while the diffusive mobility of H_2O molecules in cesium solutions appears increased relative to water, cation-water complexes exist in which H_2O molecules may vibrate many times prior to their relaxation. However, at higher concentrations the variations with anions in both the inelastic frequencies and in the Γ vs. K^2 curves appear smaller for CsCl and CsBr than for the corresponding potassium salts (compare Figures 9 and 8). With increasing concentration the curves of Γ vs. K^2 initially increase and lie above water. However, in correspondence with the inelastic frequencies, a "saturation behavior" occurs above 4.6 m for CsCl and above 2.5 m for CsBr   and little variation in Γ vs. K^2 occurs with further concentration increases. A similar behavior in the values of self-diffusion coefficients obtained from NMR measurements and diffusion data at $0°C$ has been reported by Endom et al[18].

The above results indicate that in cesium salt solutions, while the large Cs^+ ion is able to strongly disrupt the water structure and increase the average diffusive mobility relative to H_2O and KCl, it may also form ion-water complexes which are primarily cation and only secondarily anion-dependent. In contrast to cesium solutions, the anions in KCl and KBr may have a greater influence relative to the cation in disrupting the solvent structure and, hence, adding H_2O's to orient about the cation. Further, even though the primary cation-water coordinations may be weaker than for K^+ ions, the large size of the Cs^+ ions may geometrically allow them to accommodate more primary H_2O's and, hence, to more effectively compete at higher concentrations with a weak -1 anion.

With increasing concentration of cesium salts, a "saturation point" is reached such that most of the solvent structure is disrupted and the majority of the H_2O molecules are oriented by the cations. The larger Br^- (relative to Cl^-) and a weaker degree of ion-pairing in CsBr than in CsCl could both favor a stronger disruption of the solvent and a more complete hydration at a lower concentration in CsBr. The similarity of the intermolecular frequencies and of the Γ vs. K^2 curves in CsCl and CsBr at higher concentrations suggests that the frequencies and the diffusive mobility become primarily determined by the cation. Thus, at $1°C$ and at higher concentrations, the large Cs^+ ions disrupt the water structure and form cation-water complexes which have stronger bonding than solvent-solvent interactions for pure water and anion-water coordinations in the solution, but the average number of bonds may decrease. Hence, the intermolecular frequencies are primarily determined by the cation-water complexes but the D is increased and the τ_0 decreased relative to water in accord with a "negative hydration." Further, increasing the concentration reduces secondary H_2O-H_2O interactions and leads to more complete primary hydration layers. However, the binding of an H_2O molecule may be the same in a partially or completely hydrated complex and, hence, Γ vs. K^2 (and the values of D and τ_0) tend to saturate and show little change.

The temperature dependence of the inelastic spectra and of Γ vs. K^2 for CsCl solutions (Figures 6 and 10) should also be compared with those for KCl (Figures 11 and 10). At $1°C$ the spectrum of CsCl shows frequencies characteristic of ion-water complexes which sharpen with increasing temperature. In contrast, the spectrum of a 4.6 m KCl solution shows many frequencies similar to water at temperatures below $25°C$. However, above $25°C$ in KCl, new (non-water) frequencies rapidly become prominent and then persist with increasing temperature. For CsCl and KCl at $1°C$, Γ vs. K^2 lie above that for water in correspondence to increases in the D's and reduction in the τ_0's relative to water (a "structure-breaking" behavior). By $25°C$, Γ vs. K^2 for KCl lies below that for water, while that for CsCl nearly coincides with the curve for water. Hence, between $0°C$ and $25°C$ for both these

salts, a trend is observed such that the reorientational and diffusive freedom, initially greater than water, become comparable to or more restricted than in water. Identical trends have been observed by Endom et al[18] in the temperature behavior of self-diffusion coefficients as determined by spin-echo measurements. This trend with temperature also becomes more pronounced with increasing concentration such that the curve for 9.6 m CsCl, which lies close to that of 4.6 m at $1°C$, lies significantly below it at $75°C$ (Figure 12). Such behavior, as previously noted,[19] is in keeping with a decrease in the structure-breaking effect of these ions with increasing temperature, resulting from a more rapid thermal breakdown of the water-water coordination than of the primary ion-water coordinations.

It has been argued[20] from apparent molal heat capacities that the thermal decomposition of the $Cs-H_2O$ hydration complex is not appreciable until $100°C$. In contrast, the smaller K^+ ion (comparable in size to an H_2O) is not as effective as the larger Cs^+ in disrupting the solvent structure nor is its field sufficiently strong (as for small- and/or highly-charged ions) to disrupt the solvent structure. Indeed, it has been suggested[21] that the anions in potassium salt solutions may be primarily responsible for disrupting solvent structure. Thus, below $25°C$ hydrated ions may coexist with regions of solvent having an ordering that would be similar to that for water at a higher temperature. This could account both for the persistence of H_2O frequencies (Figure 11), and the fact that the increase in D, and the reduction in τ_o are small relative to water.

However, by $25°C$, the H_2O-H_2O bonding has become further weakened so that any "water-like" regions break down and the coordinations of all the H_2O molecules become primarily determined by the ions and, hence, frequencies of ion-water complexes appear and the values of D and τ become less and greater than those for water.

The results for KSCN (Figure 10) can also be understood in comparison to KCl in terms of the above arguments. At $1°C$, Γ vs. K^2 lies above both that for water and that for KCl, and unlike KCl, new frequencies appear in the inelastic regions which are different than those of water and are characteristic of ion-water frequencies. Thus, the SCN^- in the KSCN solution appears to have disrupted the solvent structure at $1°C$ and the orientation of the solvent molecules is determined by their coordinations to the ions. In contrast, as it appears that Cl^- is less effective in disrupting the solvent than SCN^-, the solvent is not strongly disrupted

11

in the KCl solution until about 25°C, as will be discussed below. With increasing concentration at 1°C (Figure 12), the difference in the curves of Γ vs. K^2 for KSCN and H_2O decreases and the curve for KSCN approaches that for water. Simultaneously, the inelastic frequencies persist but become better resolved and defined. These spectral changes are thus in accord with the increase in the relative number of primary ion-water coordinations for which the ion-water bonding has a similar strength to that in pure water.

In addition, for KSCN, with increasing temperature, Γ vs. K^2 approaches that for water and then falls below the curve for water. Its behavior reflects an increase in primary hydration with increasing temperature, as discussed above for CsCl. Correspondingly, the ion-water inelastic maxima also sharpen and become better defined with increasing temperature.

Evidence has been cited[8] for the possible existence of a "transition" (near 22°C) in KCl solutions. The derivative of the solubility with temperature[22] shows a second order transition at about 22°C. X-ray diffraction measurements[23] indicate the coexistence of both ion-water coordinations and "water-like" regions below 22°C, but a more homogeneous distribution of the H_2O molecules above 22°C. Further, Hertz et al[18] report that, at temperatures below about 25°, the self-diffusion coefficient for KCl solutions is slightly larger than for water, and KCl thus acts as a "structure breaker." At higher temperatures the reverse is true and KCl acts as a "structure maker." In this regard, it is of interest to note that the observed temperature dependence of the width of the quasi-elastic maximum and the associated diffusive kinetics show a discontinuous change near 29°C for a 4.6 m KCl solution. As previously reported at[1] lower temperatures, a delayed diffusion model appears to be adequate to explain the shape, and the dependence of the observed width on K^2 and on temperature. However, for most solutions a temperature is reached whereby at higher K^2 values "free-particle" motions[24] may also contribute. In general, for solutions of ions which act as "positive hydrators" this temperature is higher than for water, while for ions causing "negative-hydration" it is lower. To examine this temperature behavior it is convenient to express the observed dependence of

Γ vs. K^2 in terms of the dimensionless parameters [1][24]

$$\Gamma/kT = y \quad \text{and} \quad \hbar DK^2/kT = x,$$

for a series of temperatures (Figure 13).

At smaller values of x the values of y fall on the y = x line as expected for the classical diffusion limit, but at larger x values the curves fall below this line. Between $1°C$ and $25°C$ at larger values of x, the values of y are observed to increase in a regular manner with temperature, in accord with jump-diffusion for which

$$y = \frac{\hbar}{\tau_0 kT} \left[1 - \frac{e^{-2W}}{1 + \frac{kT\tau_0}{\hbar} x} \right]$$

At large x values, $y \longrightarrow \frac{\hbar}{\tau_0 kT}$ (as the residence time decreases exponentially with increasing temperature, y would increase). However, y vs. x abruptly decreases at $30°C$ and indeed all the y vs. x curves above $30°C$ are systematically low. Above $30°C$ the y vs. x curves again increase with temperature. The decrease in y near $30°C$ could be associated with the onset of contributions from "a free particle" diffusive motion of characteristic time, $\tau_g = \frac{MD}{kT}$ which is comparable to the neutron interaction time. M would correspond to the net mass of a number of molecules moving in a correlated manner and would approximately correspond to about 80 to 100 H_2O's (i.e., 5-6 ions and their hydration layers). The rise in the y vs. x curves above $30°C$ with temperature would correspond to a loss in correlation and, hence, to a decrease in M, so that τ_g would become short compared to the interaction time and, hence, a delayed diffusion behavior would again be observed. A decrease in y near transition temperature could also occur if a sudden change in the jump diffusion parameters results from a change of solution structure. While the above explanations must be considered tentative, they can provide a plausible and consistent explanation for the observed changes in the solubility, x-ray and neutron data. At lower temperatures the weakly-hydrated ions may be spanned by

regions of the solvent with a local ordering similar to water and diffusion would mainly be due to activated jumps of individual molecules with an average activation energy lower than that for water. Near the transition temperature the thermal excitation may be sufficient to break the weaker bridging bonds, decouple the hydrated ions and allow correlated motions of large groups of ions and H_2O molecules to occur more freely. With increasing temperature, a further reduction in the number of bridging bonds, in the size of the higher hydration layers, and in the correlation would occur.

IV. DISCUSSION

The variations of the intermolecular frequencies and the diffusive kinetics observed in this NIS investigation and their interpretation are in reasonable agreement with other reported theoretical and experimental results. Evidence has been cited that in more dilute aqueous ionic solutions "remnants" of water structure can persist. Further, it appears that hydration complexes may affect the more distant solvent structure beyond the primary layer in a manner specific to the size and charge of the ion. It is not to be implied that such a "water-like" solvent structure is necessarily in exact correspondence to the pure solvent. It may be strained or perturbed. Rather it is implied that a complete disruption has not occurred and the solvent structure, first and higher neighbor O---O distances, relaxation times, and activation energies are similar to those for water. Thus, Samoilov[8] has argued that for dilute solutions the hydration of ions takes place with a minimum modification of the distant water structure. He noted that although the interaction energy of an ion with H_2O molecules not in its primary hydration layer may be very small, the total energy obtained from the summation over many such molecules may be significantly large and correspond to a considerable part of the heat of hydration. Fabricand et al[25] found that the solvent far from the hydrated ions has a proton

relaxation time similar to that of pure water. Also, x-ray results[26] have indicated that, for dilute solutions, maxima can persist at the same positions as those of water.

Hindman[16] pointed out that the primary layers for most +1 cations, with the exception of Li^+, were not fully hydrated and their fields were insufficient to reorient H_2O molecules beyond the first layer. It thus appears improbable that structural modifications and large dipole reorientation could occur due to the ionic fields penetrating into the bulk solvent (far from the ions). Rather, he has suggested that the field component in the bond direction of the primary waters may effectively redistribute the charge on the water protons and give rise to a degree of polarization that could penetrate into the bulk and serve to alter the effective "structural temperature" of the distant solvent. Zunbel and Murr[27] have also argued from IR results that strong and partially covalent coordinations between a cation and primary waters could cause a polarization and increase the hydrogen bond strength between primary hydration layer and the surrounding H_2O's.

Recently Tikhomirov[10] has also considered the effect of ions on the distant or "free" water, taking into account the earlier work of Samoilov[8] and Hindman[16]. He points out that the water molecules in the immediate vicinity of the ions can be strongly reoriented relative to water, and coordinated in a manner specific to the cation. This creates an intermediate region of structural misfit between the primary hydration coordinates and the distant solvent. The intermediate water molecules will reorient to accommodate themselves between these two different structures. In general the average number of bonds per water molecule will be reduced, in this region, relative to water. However, the reduction in the average number of bonds can be countered by the polarization of the primary water molecules by the cation. Thus, the hydrogen bonding between molecules in the solvent is reinforced by the ion-field component in the bond direction which effectively lowers the

temperature of the solution. Further, Takomirov suggests that such polarization effects may be transmitted beyond the second and third hydration layers. The more covalent the primary cation-water interaction, the stronger are the deformations of charge on the H_2O molecules on the primary layers and further is the "transmission" of such polarization effects. Both the orientation effects of a cation on the primary water and the polarization, would decrease with decreasing charge-to-radius of a cation. Whether the molecules in the "intermediate region" are more or less mobile than in normal water depends upon whether the reduction in the number of bonds due to the structural misfit has been compensated by such polarization effect.

Hasted and Roderick[28] from dielectric relaxation measurements also have argued that the field of most singly-charged ions is, in general, only large enough to break bonds and orient molecules in the first layer, whereas, larger, highly-charged ions, like Ba^{+2} and La^{+3}, may reduce the number of H bonds but give rise to irrotational water molecules in the second hydration layer.

For a given charge-to-radius ratio the size of a cation may play a role in increasing the structure-breaking in the intermediate region due to mismatch. Thus, Glueckauf[29] has reported that the "electrostriction volume" is a function of the charge and radius of the ion and as the radius increases the electrostriction field would decrease but the electostriction volume may still be large. However, it has been pointed out that Li^+ has an abnormally small electrostriction volume. If a cation, like Li^+, is small and only a few primary water molecules are rigidly oriented about it, water molecules in the intermediate layers may have to reorient significantly from the original water structure to couple to this primary complex. The "strain energy" resulting from such a structural mismatch may serve to disrupt water structure for a significant distance from the primary layer. In contrast, if the cation is large, so that many waters may be oriented around it with their protons pointing out, then the surrounding water molecules need to reorient only slightly for coupling.

16

As the concentration is increased the ions act upon a decreasing amount of free water, the cation-anion separation decreases and the probability of an ion-pairing increases either directly or through the intermediary of primary hydration waters about the cation. In general, the probability of direct ion-pairing increases with concentration and cationic size and decreasing anionic size. In alkali-halide solutions appreciable ion-pairing has been reported[16][30] only for the cesium and rubidium halides. Lawrence and Kruch[30] have pointed out that such ion-pairing would result in regions occupied by aggregations of ions and others dominated by solvent-solvent interactions. These observations are thus in accord with the concentration behavior discussed above for CsCl and CsBr where the relative number of primary Cs^+-H_2O coordinations is, at a given concentration, larger in CsBr than in CsCl solutions.

Bryant[31] and Wossner[17] have reported abrupt changes in the relaxation rates for H_2O molecules and Li^+ ions as the concentration of LiCl solutions is increased above about 4.4 m. They noted that above this concentration the lithium ion becomes less effective in slowing down water molecules in its vicinity, possibly due to changes in the symmetry of the lithium ion-water complex. At these concentrations such changes may arise from variations in the second hydration sphere or from indirect ion-pairing through the primary hydration waters. As shown in Figure 4 , the inelastic spectra for LiCl solutions vary strongly between 1 m and 4.6 m. However, only smaller variations occur at concentrations of 4.6 m and 15.2 m where frequencies, characteristic of the cation-water complexes with a local ordering similar to that observed in the solid hydrate , have been reported.

The present data for the cesium and potassium salts are in accord with the observation by Hindman[16] that large, singly-charged ions (i.e., Cs^+) may form hydration layers while still effectively breaking "water" by loosening its coordination in the intermediate regions. At lower temperatures the "boundary-line" between structure-breaking and -making cations is generally accepted to occur between Na^+ and K^+ in accord with the

dependence of the Γ vs. K^2 curves on cation, as shown in Figure 8 . However, there exists ample evidence[18][19][32] that the structure-breaking and -making effects vary with both concentration and temperature, in the manner observed in the present investigation. M. Kaminsky[32] has pointed out that the ordering of H_2O molecules in the vicinity of strongly-hydrating ions like Be^{+2}, Mg^{+2} and Li^{+1} becomes increasingly disturbed and diminishes with increasing temperature. Indeed, previously reported results[1] and the results of the present investigation support such a behavior. In like manner, Ionov[19], from nuclear quadruple relaxation measurements, argued that above $50°C$ all alkaline metal cations retard the Brownian rotation of water molecules and act as "positive hydrators." However, at $50°C$, none of the salts, CsCl, KCl, NaCl and LiCl, produce an increase in the rotational freedom of water molecules relative to pure water, and at $90°C$ these salts only decrease the relative rotational freedom. Thus, as the solvent structure is thermally disrupted an increase in the solvation occurs. Also, Endom et al[18], from spin-echo measurements of the self-diffusion coefficients of H_2O molecules in aqueous solutions, have reported that certain salts (i.e., KCl, KBr, KI, CsCl, CsBr), at low temperatures (typically $1°C$ and $25°C$), show a structure-breaking tendency. In contrast, at higher temperatures they show a structure-making tendency such that the self-diffusion coefficients are less than that for water. At $0°C$ a certain concentration is reached above which the self-diffusion coefficient in the presence of a structure-breaking cation such as Cs^+ no longer increases relative to water (becomes nearly constant), and may even slightly decrease again. Thus, in accord with the present results, a "saturation" is observed in the structure-breaking behavior of such salts with concentration. This would indicate that the coordinations of the H_2O molecules in the primary hydrations of the cation would be stronger than in those further removed regions in accord with Hindman's observation[16] that such ions may form primary hydration complexes while still decreasing the solution viscosity. Indeed, the results of the present investigation for KSCN solutions

18

constitute a similar but pronounced example. A reversal from a "structure-breaking" to a "structure-making" behavior occurs with increasing concentration.

It is generally accepted that anions such as Cl^{-1}, I^{-1}, NO_3^{-1}, ClO_4^{-1}, Br^{-1} increase the diffusion coefficient and act as "structure-breakers" or "negative hydrators." Solovkin[33] has noted that NO_3^- ions act as "negative hydrators" or "structure-breakers" in the presence of all cations and to a larger degree than Cl^- ions. Further, on the basis of activity coefficients, he has found that in the presence of large +1 cations (i.e., Rb^+ and Cs^+) the surface density of waters for Cl^-, Br^-, I^- and NO_3^- is nearly independent of the cation and increases with the radius of the anion. In contrast, in the presence of smaller cations such as Na^+ and Li^+ the surface density of waters about the anion varied with the cation.

Andreev[34] has noted that in 2 molal LiCl and LiNO₃ solutions both the diffusion coefficients for the lithium cation and for the H_2O's are unaffected within a percent by the replacement of Cl^- ions by NO_3^- ions. Frank and Evans[35] have suggested that the NO_3^- ion may approach and disrupt the water of hydration about a cation more strongly than a Cl^- ion. Such a behavior is similar to that observed by Cannon and Richards[36] and by Hester and Grossman[37] who report that in indium-nitrate solutions the NO_3^- ion may cause fluctuating field gradients near the region of primary hydration and displace a small number of water molecules in the primary layers. Any degree of true ion-ion contact would, of course, be extremely small in view of the strong covalent bonding between the cation involved and the primary water molecules. These results are in keeping with the observations of the present experiment that for concentrated nitrate solutions of strongly hydrating cations such as La^{+3} and Li^+, strong primary cation-water coordinations are formed and the NO_3^- ion, relative to Cl^-, tends only slightly to disrupt the cation-water complexes, broaden the characteristic frequencies and increase the associated values of D and decrease the values of τ_0.
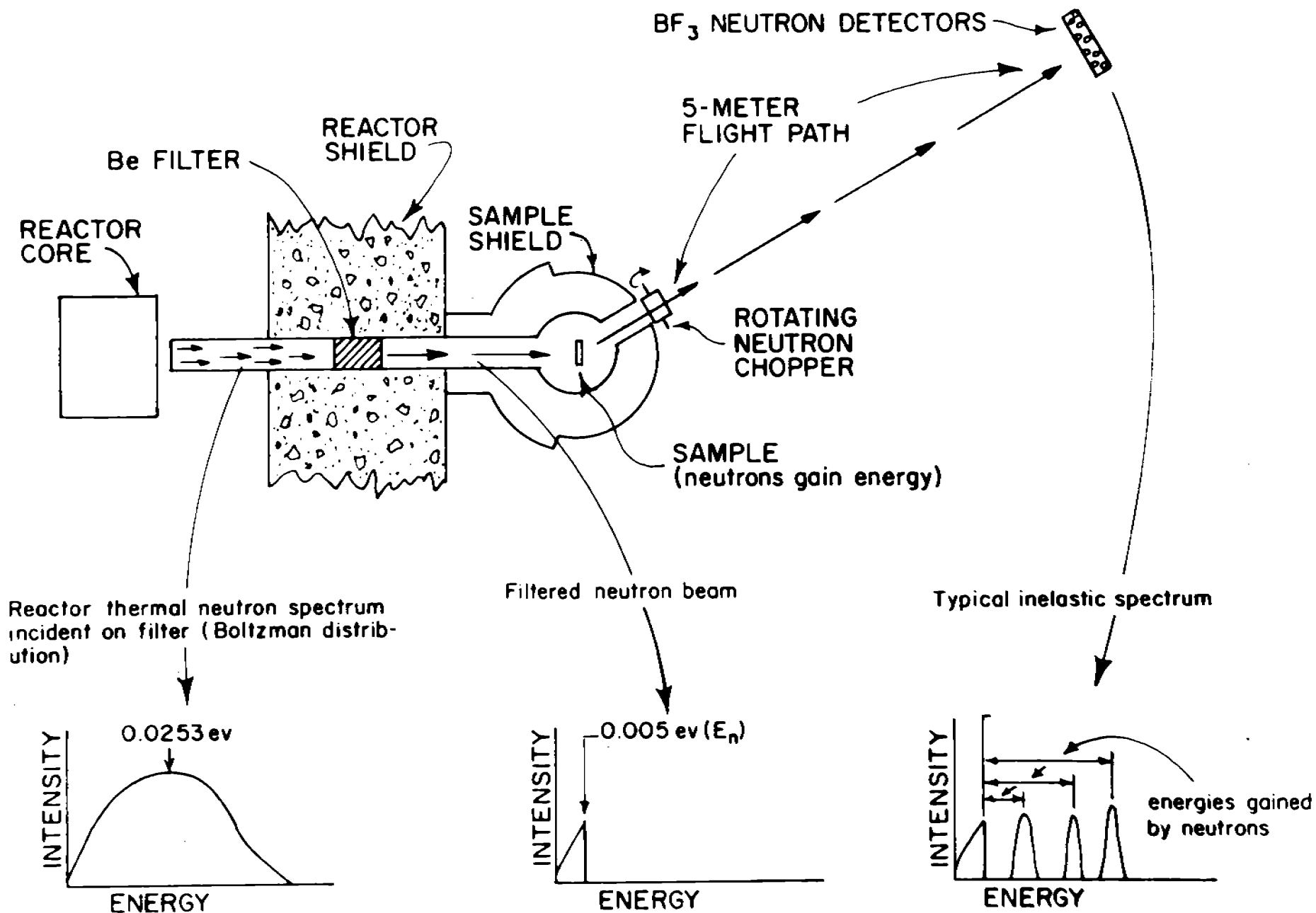
This behavior implies (especially for the small- and/or highly-charged cations) stronger cation-water than anion-water interactions. Thus, Hindman[16] has noted that the high density of negative charge in the H_2O molecule associated with the lone pair regions could provide a larger interaction energy between the water molecule and a cation than between the water molecule and an anion of equal radius. Further, Syrnikov[38] has calculated, by the molecular orbital method, the fraction of the energy of interaction between ions and water molecules associated with quantum mechanical effects for alkali metal cations and halide anions. He showed that the energy of delocalization of electrons upon hydration decreases in going from lithium to cesium in the cations, and the interaction is smaller for the anions than for the cations. Also, x-ray studies of solutions of lithium and erbium chloride have suggested that the Cl^- ions are disposed in a fairly regular manner outside the primary hydration layer of the cations in the solutions. Brady[39] has suggested from x-ray diffraction studies of lithium-chloride solutions that the hydration of the Cl^- ions may not be "true" in the sense that their ionic fields may not be sufficiently strong to withdraw solvent molecules from the liquid pseudo lattice and realign them around the anions.

In contrast to salts with small- and/or highly-charged cations the observed NIS spectra of intermolecular frequencies, the self-diffusion coefficients, and the residence time for the potassium salts are more strongly anion-dependent. Further, Raman frequencies assigned to anion-water coordinations are observed in the NIS spectra. It would thus appear that larger -1 halide ions may be polarized by the solvated water molecules in a manner that leads to a water-anion bond which is slightly weaker than the hydrogen bond in water and the primary cation-water inter-actions. Further, in contrast to the K^+ cation (which has similar size to a water molecule), a still larger ion like Cs^+ could accommodate more H_2O's in the primary layers where the bonding could still be stronger than primary anion-water coordinations. Such an effect would tend to reduce differences with anions.

20

FIGURE 1

Schematic diagram of Neutron Inelastic Scattering
Spectrometer.

BF$_3$ NEUTRON DETECTORS

5-METER FLIGHT PATH

REACTOR SHIELD

Be FILTER

SAMPLE SHIELD

REACTOR CORE

ROTATING NEUTRON CHOPPER

SAMPLE (neutrons gain energy)

Reactor thermal neutron spectrum incident on filter (Boltzman distribution)

0.0253 ev

INTENSITY

ENERGY

Filtered neutron beam

0.005 ev (E$_n$)

INTENSITY

ENERGY

Typical inelastic spectrum

energies gained by neutrons

INTENSITY

ENERGY

FIGURE 2

The neutron time-of-flight spectra measured at $1°C$ and a scattering angle of $45°$ for dilute solutions of LiCl, $MgCl_2$, CsCl and NaCl and for a 4.6 m solution of KCl (at $15°C$) are compared with the water spectrum at $25°C$. The vertical lines show the peaks in water spectrum which occur in solutions at nearly the same frequencies. The frequencies in parenthesis are from Raman measurement[40] and that in brackets are from another NIS measurement[41]. In this and the following figures, the statistical errors, as calculated from the total and background counts, are represented for comparison with the spectra by the solid strip at the top of the figure. At a given channel, the full width of the strip extends from +1 to -1 standard deviation, σ.
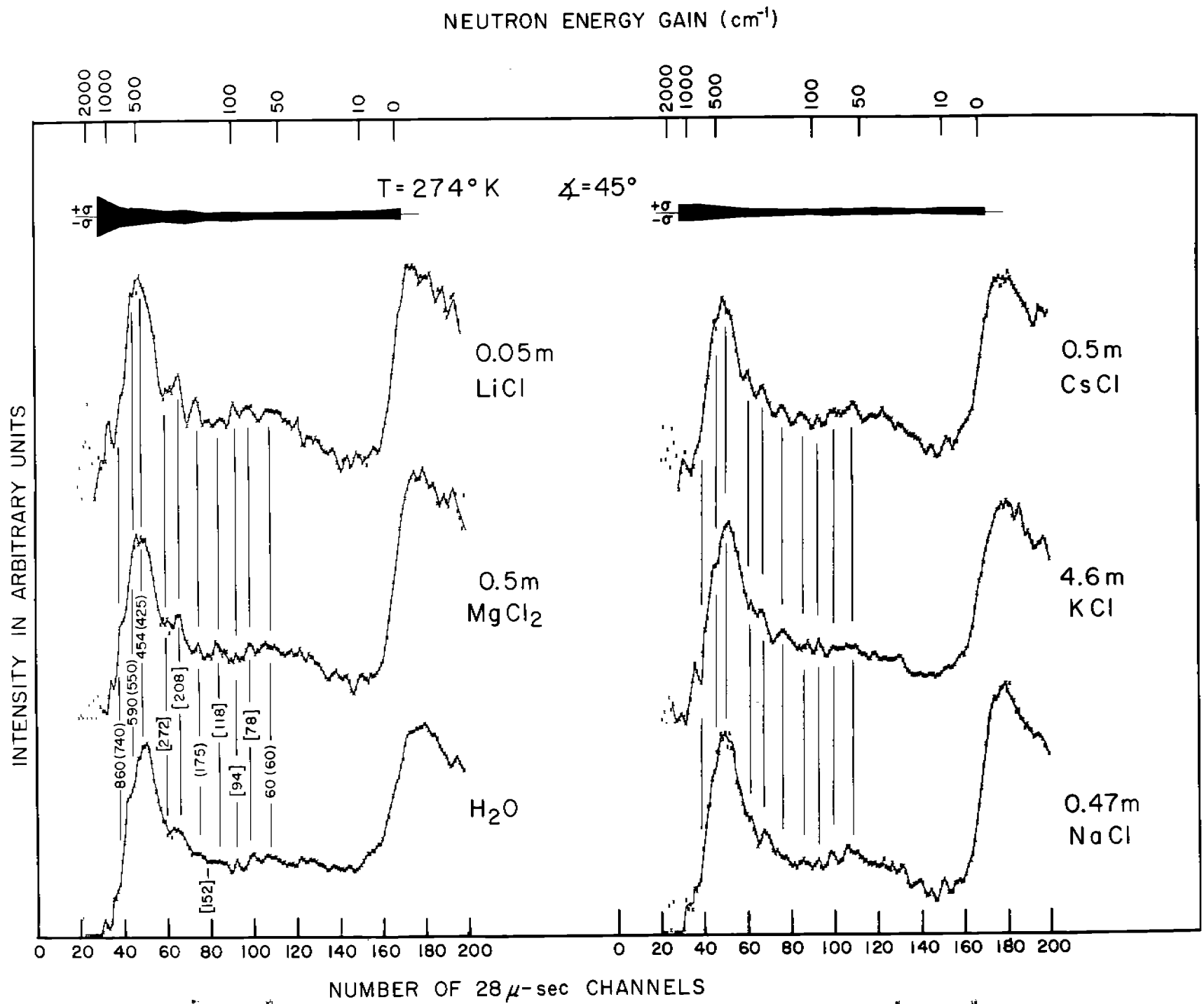
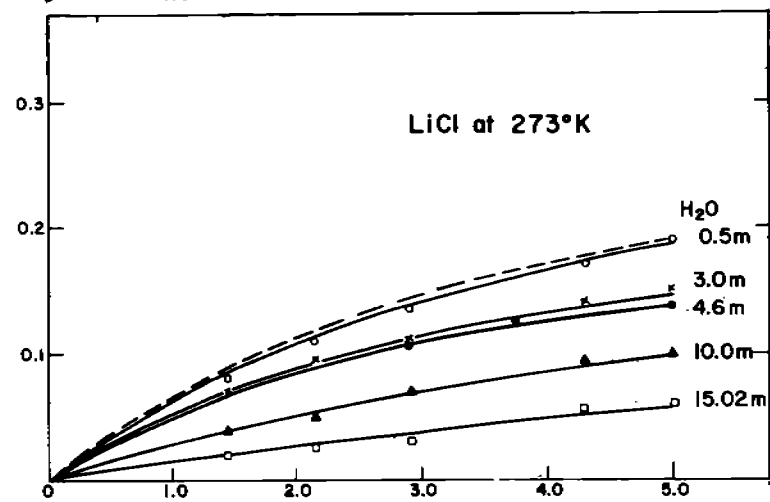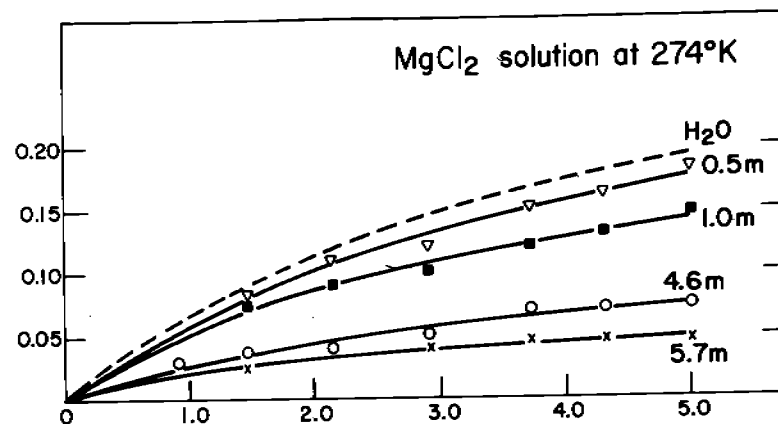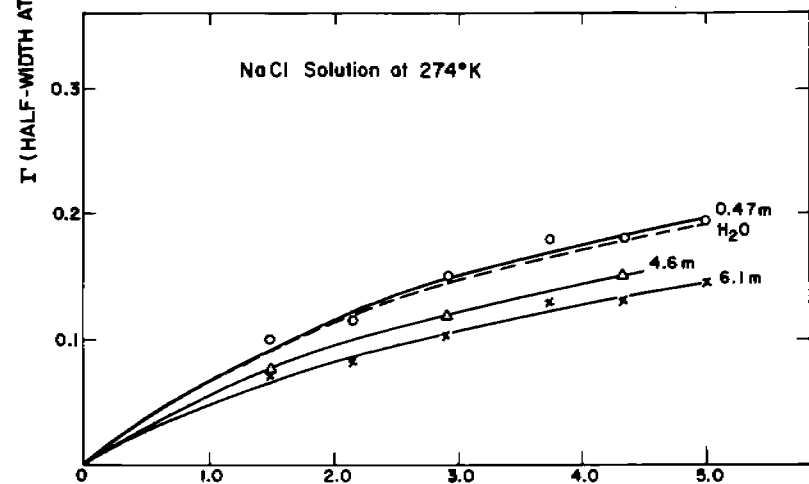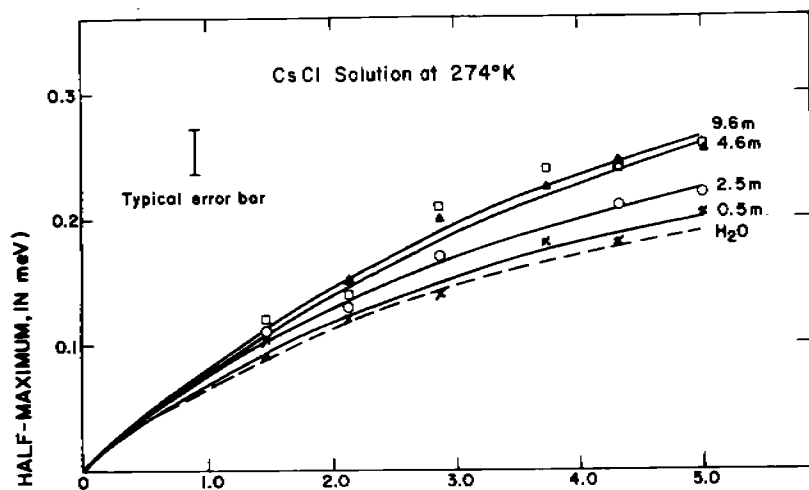NEUTRON ENERGY GAIN (cm⁻¹)

NUMBER OF 28μ-sec CHANNELS

FIGURE 3

The Lorentz half-widths at half-maxima, Γ, as a function of the momentum transfer squared (K^2) are shown for CsCl, NaCl, LiCl and MgCl$_2$ solutions at various concentrations. The lines through the data represent best fits using Equation 1 as given by the jump diffusion theory. The values of the residence time, τ_0, and the self-diffusion coefficient, D, are thus obtained by best fit from least squares. They are listed below. D* is the self-diffusion coefficient obtained from the slope at the origin of the curves, it would include contributions from both the jump re-orientations and large vibrational amplitudes of the bonded molecules. It is best compared to the results of tracer techniques and spin echo measurements.

		$\tau_0 \times 10^{12}$ sec	$D \times 10^5$ cm^2/sec	$D^* \times 10^5$ cm^2/sec
H$_2$O		2.4	0.8	1.2
MgCl	0.5 m	2.8	0.6	1.1
	1.0 m	3.5	0.76	1.0
	4.6 m	6.1	0.4	0.5
	5.7 m	11.1	0.37	0.46
NaCl	0.47 m	2.3	0.81	1.25
	4.6 m	2.8	0.75	1.05
	6.1 m	3.1	0.52	0.85
CsCl	0.5 m	2.2	0.77	1.2
	2.5 m	2.0	0.84	1.4
	4.6 m	1.4	0.9	1.4
	9.6 m	1.5	0.9	1.5
LiCl	0.5 m	2.4	0.75	1.1
	3.0 m	3.3	0.67	1.0
	4.6 m	3.2	0.64	0.92
	10.0 m	3.6	0.16	0.47
	15.2 m	5.0	0.0	0.21

FIGURE 4

The neutron time-of-flight spectra are shown for LiCl solutions at various concentrations. The reported frequencies from Raman[40] and IR[42] are marked with R and IR, respectively.
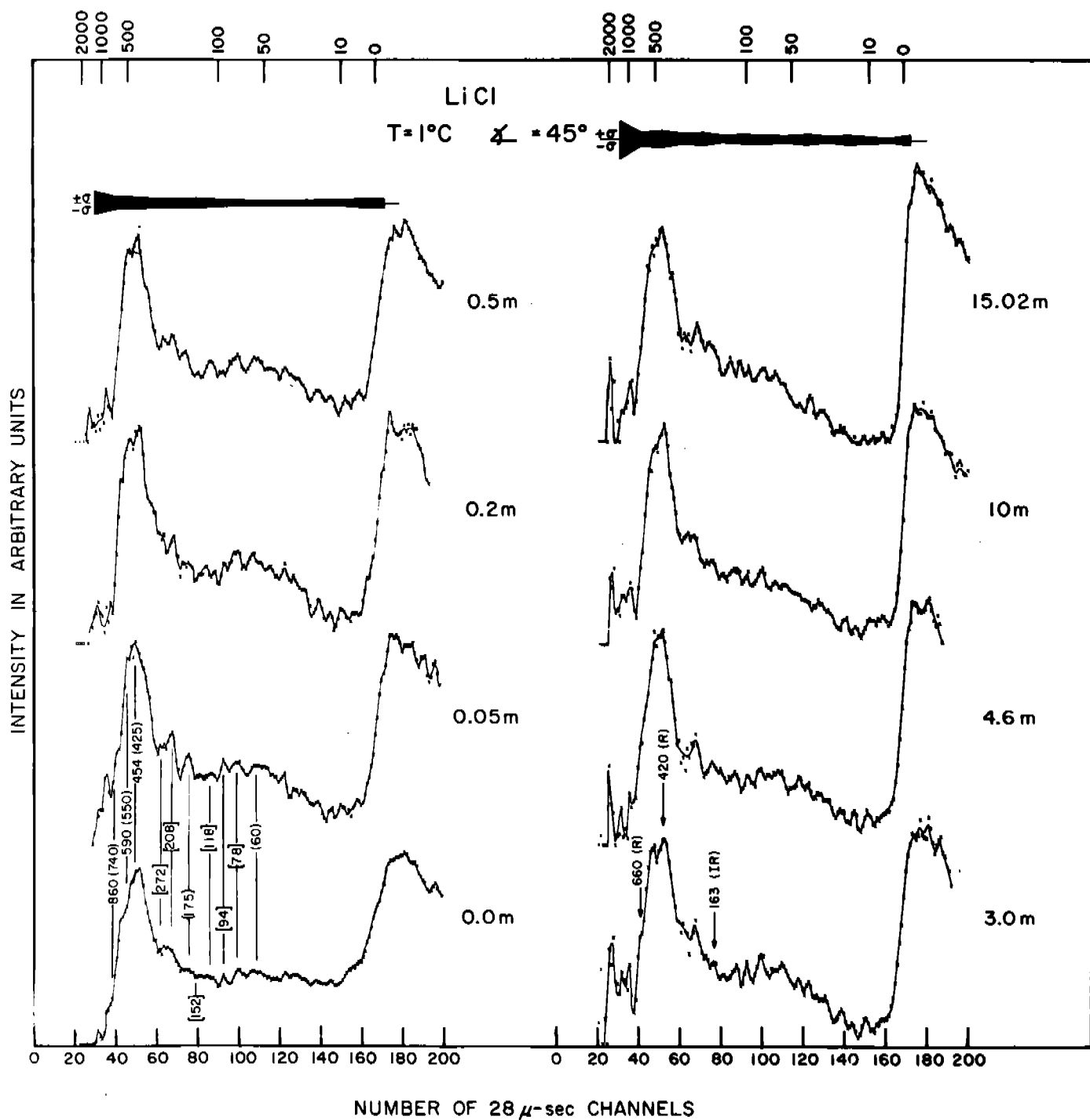
FIGURE 5

The neutron time-of-flight spectra are shown for NaCl solutions at various concentrations. The reported frequencies from Raman[40] and IR[42] are marked with R and IR, respectively.
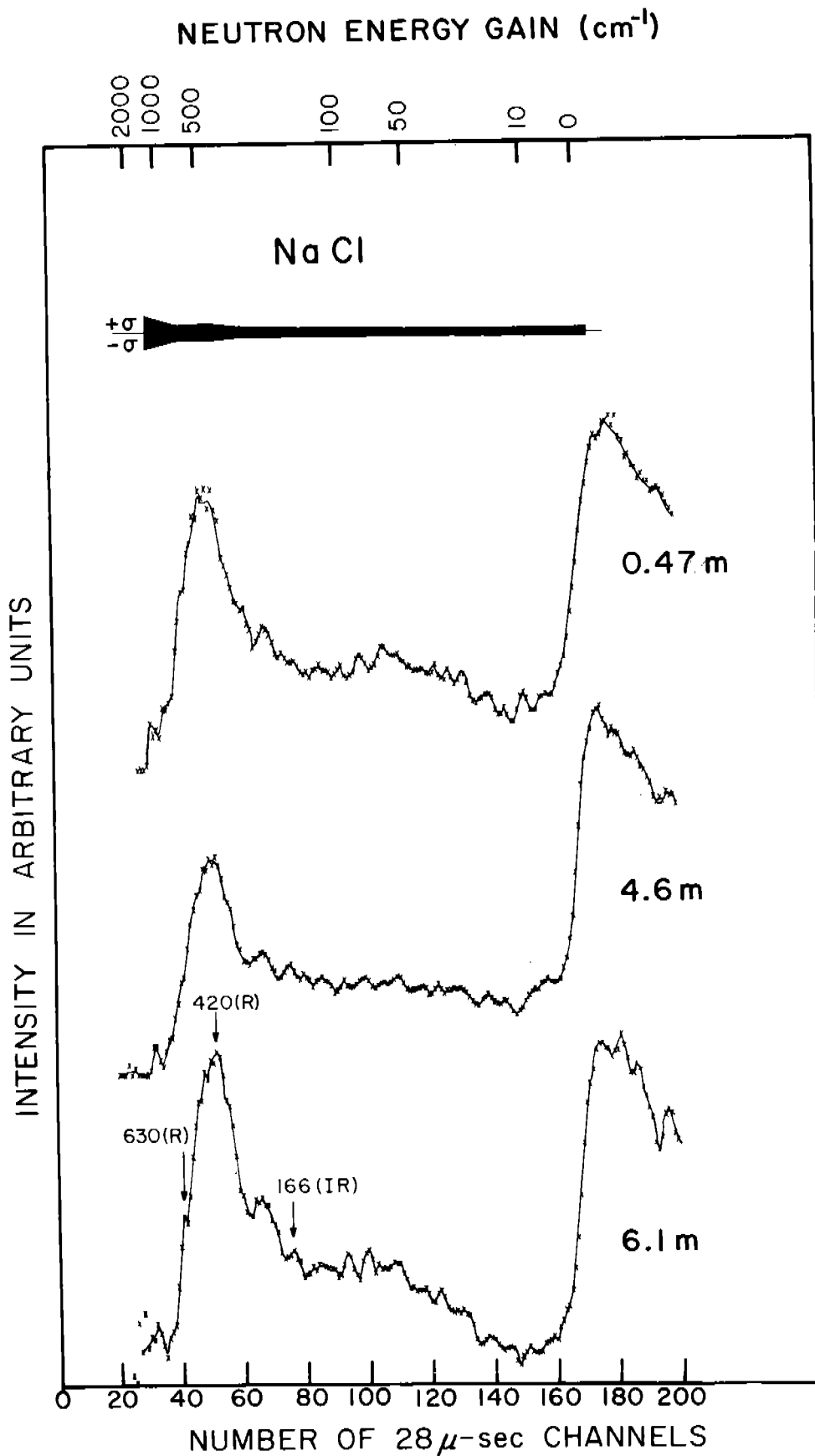
NEUTRON ENERGY GAIN (cm⁻¹)

NUMBER OF 28 μ-sec CHANNELS

FIGURE 6

The neutron time-of-flight spectra, measured at 1°C and a
scattering angle of 45° for CsCl solutions at various con-
centrations, are shown at left. Also, spectra at various
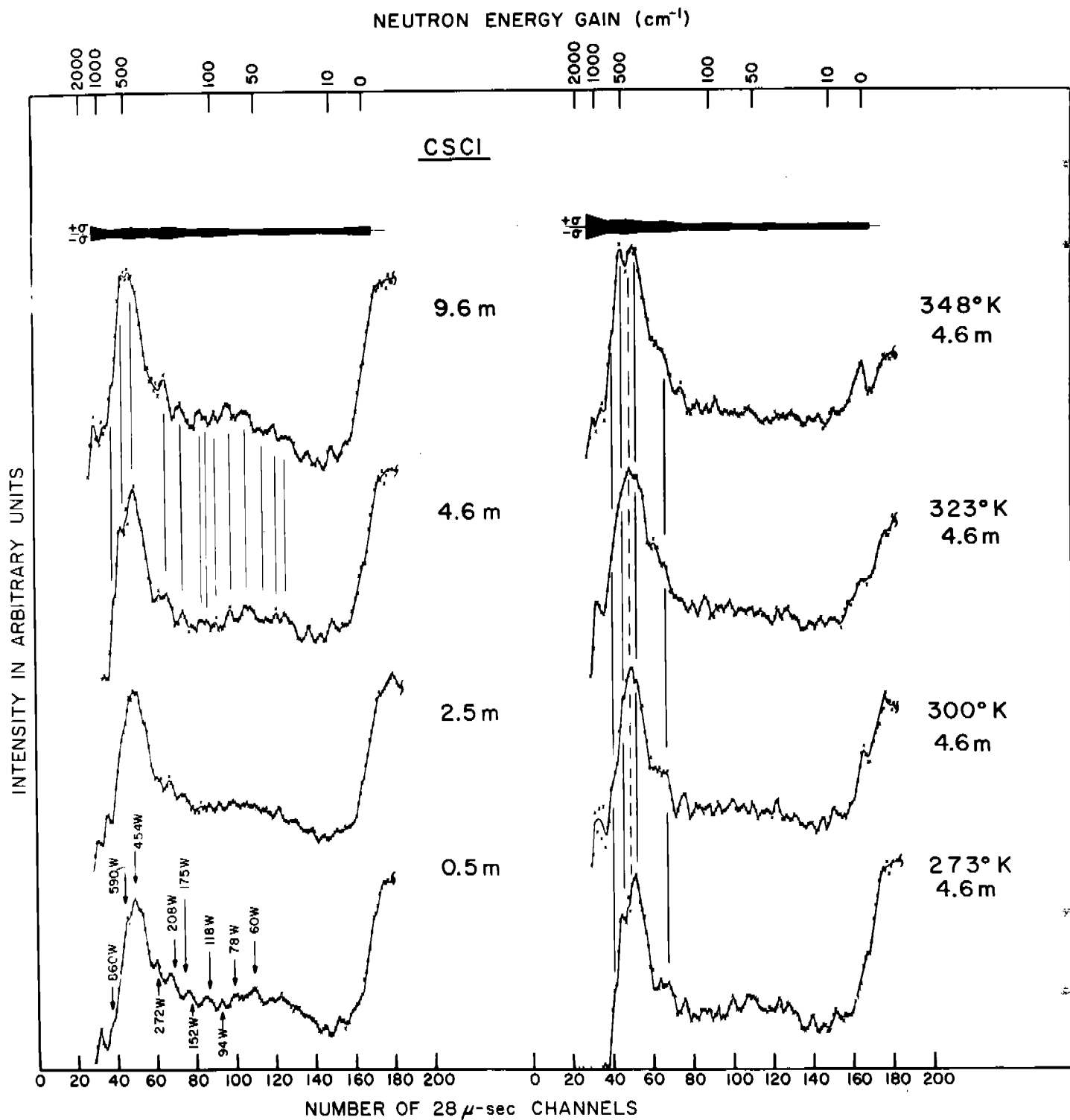temperatures of a 4.6 m solution are shown at right.

NEUTRON ENERGY GAIN (cm⁻¹)

CSCI

FIGURE 7

The neutron time-of-flight spectra for $La(NO_3)_3$ and $LaCl_3$ solutions are intercompared as are those for LiCl, LiSCN and $LiNO_3$. The Raman and IR frequencies for LiCl are from Walrafen[40] and Draegert and Williams[42], respectively. The Raman frequency for $LiNO_3$ was from Mathieu and Lounsbery[43].

NEUTRON ENERGY GAIN (cm⁻¹)

2000 1000 500   100 50   10 0   2000 1000 500   100 50   10 0

∢ = 45   T= 1°C

+σ
−σ   +σ
                                          −σ

660 (R)   420 (R)   163 (IR)

3.5 m
La(NO₃)₃   4.6 m
                                           LiCl

4.3 m
La (NO₃)₃   4.6 m
                                           LiSCN

3.5 m
LaCl₃   4.6 m
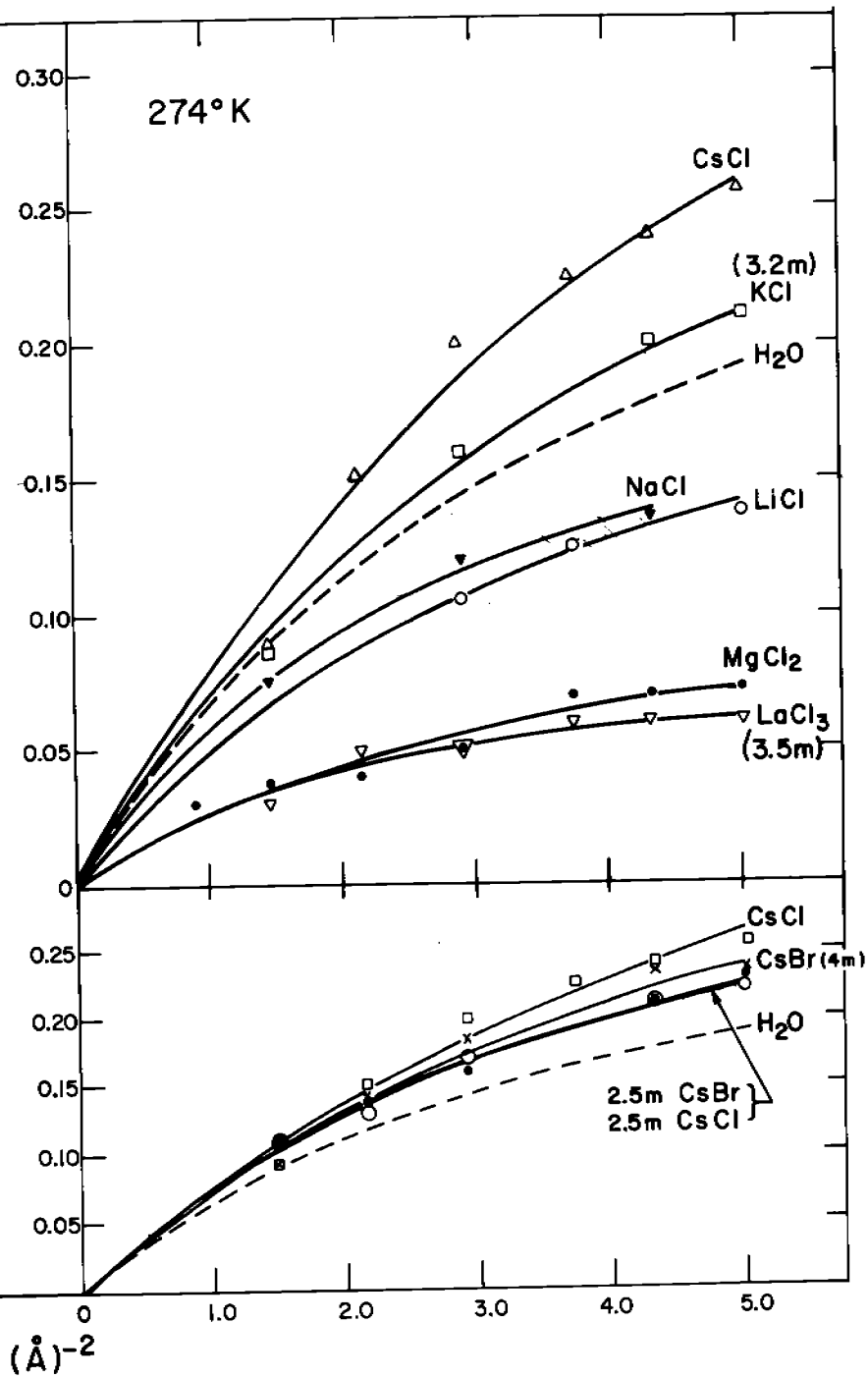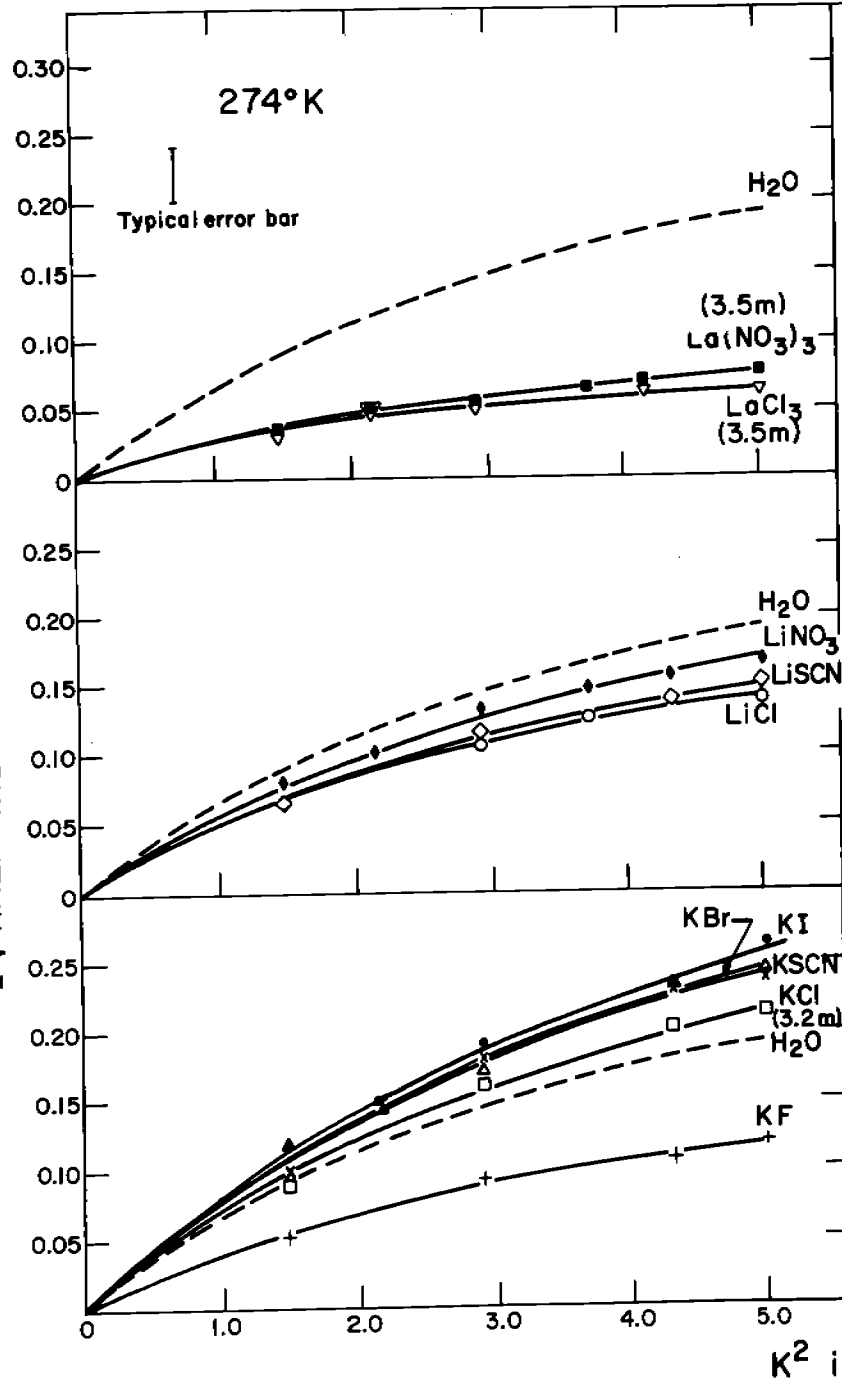   LiNO₃

720 (R)

INTENSITY IN ARBITRARY UNITS

0 20 40 60 80 100 120 140 160 180 200   20 40 60 80 100 120 140 160 180 200

NUMBER OF 28μ-sec CHANNELS

FIGURE 8

The observed Γ vs. K^2 curves are compared for a series of chloride solutions (cation dependent) and for a series of solutions of lanthanum, lithium, potassium and cesium salts (anion dependent).

FIGURE 9

The neutron time-of-flight spectra for potassium halides are
compared. The frequencies marked (R) and (IR) are those from
reported Raman[40] and IR[42], respectively. The spectra of
4.0 m CsBr and 9.6 m CsCl are intercompared. The vertical
lines show the similarity of frequencies in both spectra.

NEUTRON ENERGY GAIN (cm⁻¹)

4.6 m Solutions
273°K ∠ 45°

INTENSITY IN ARBITRARY UNITS

KF
230 (IR)
169 (IR)

650(R)
450(R)
153 (IR)
KCl
(3.2m)

660 (R)
440(IR)
149 (IR)
KBr

140 (IR)
KI

CsBr
(4.0m)

CsCl
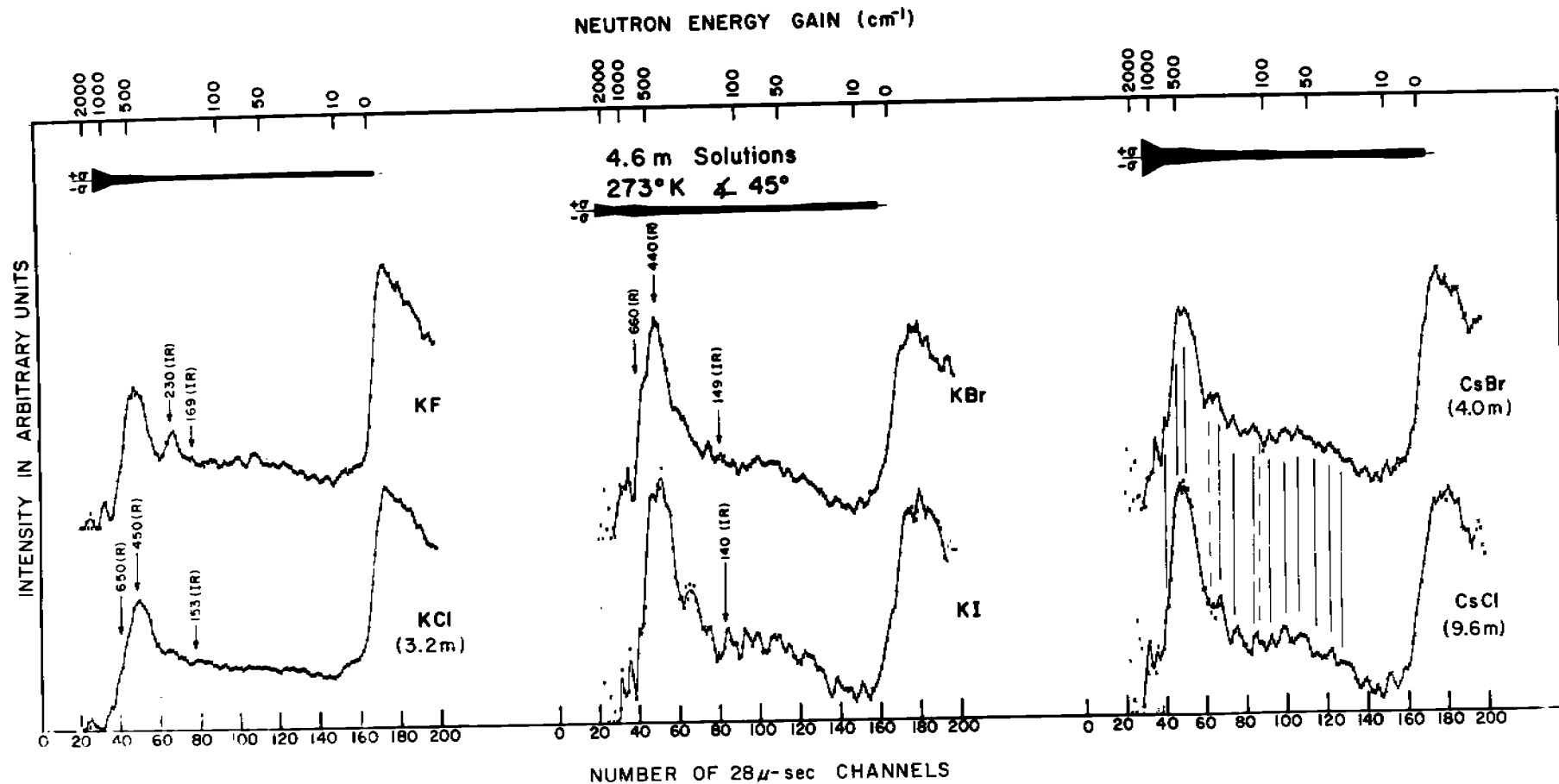(9.6m)

NUMBER OF 28 μ-sec CHANNELS

FIGURE 10

The observed values of Γ vs. K^2 are shown for water and aqueous solutions of salts having large singly-charged ions at 1°C, 25°C, 50°C and 75°C. The concentration of all the solutions was 4.6 m except for the KCl at 1°C which was 3.2 m.
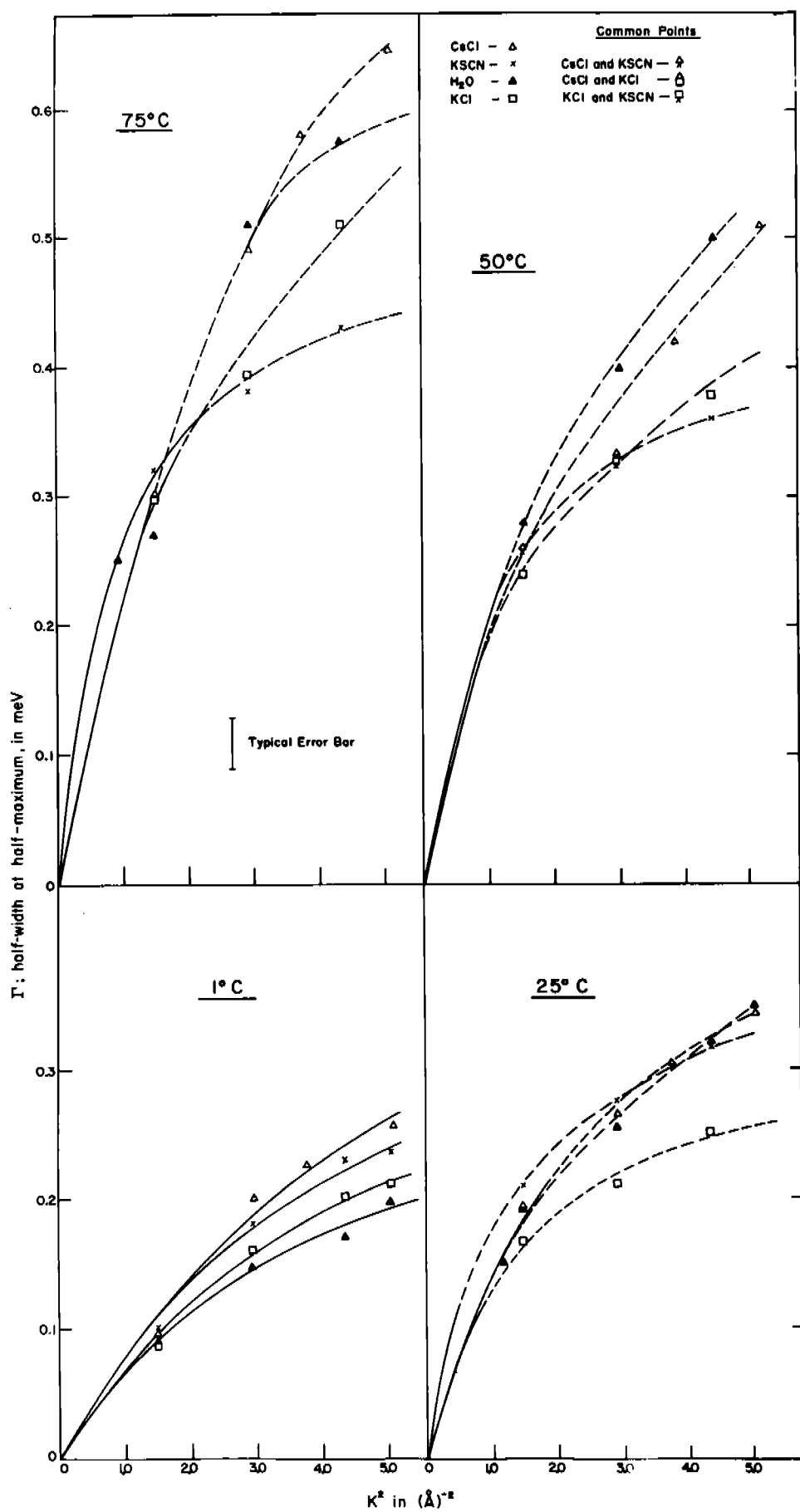
Common Points

CsCl – △
KSCN – ×
H₂O – ▲
KCl – □

CsCl and KSCN – ⬙
CsCl and KCl – ⬡
KCl and KSCN – ⊡

75°C

50°C

Γ; half-width at half-maximum, in meV

Typical Error Bar

1°C

25°C

K^2 in $(Å)^{-2}$

FIGURE 11

The neutron time-of-flight spectra for 4.6 m KCl solution
(3.2 m at 1°C) are shown at various temperatures. The frequen-
cies marked W corresponding to those for water. The Raman
and IR frequencies were reported by Walrafen[40] and Draegert
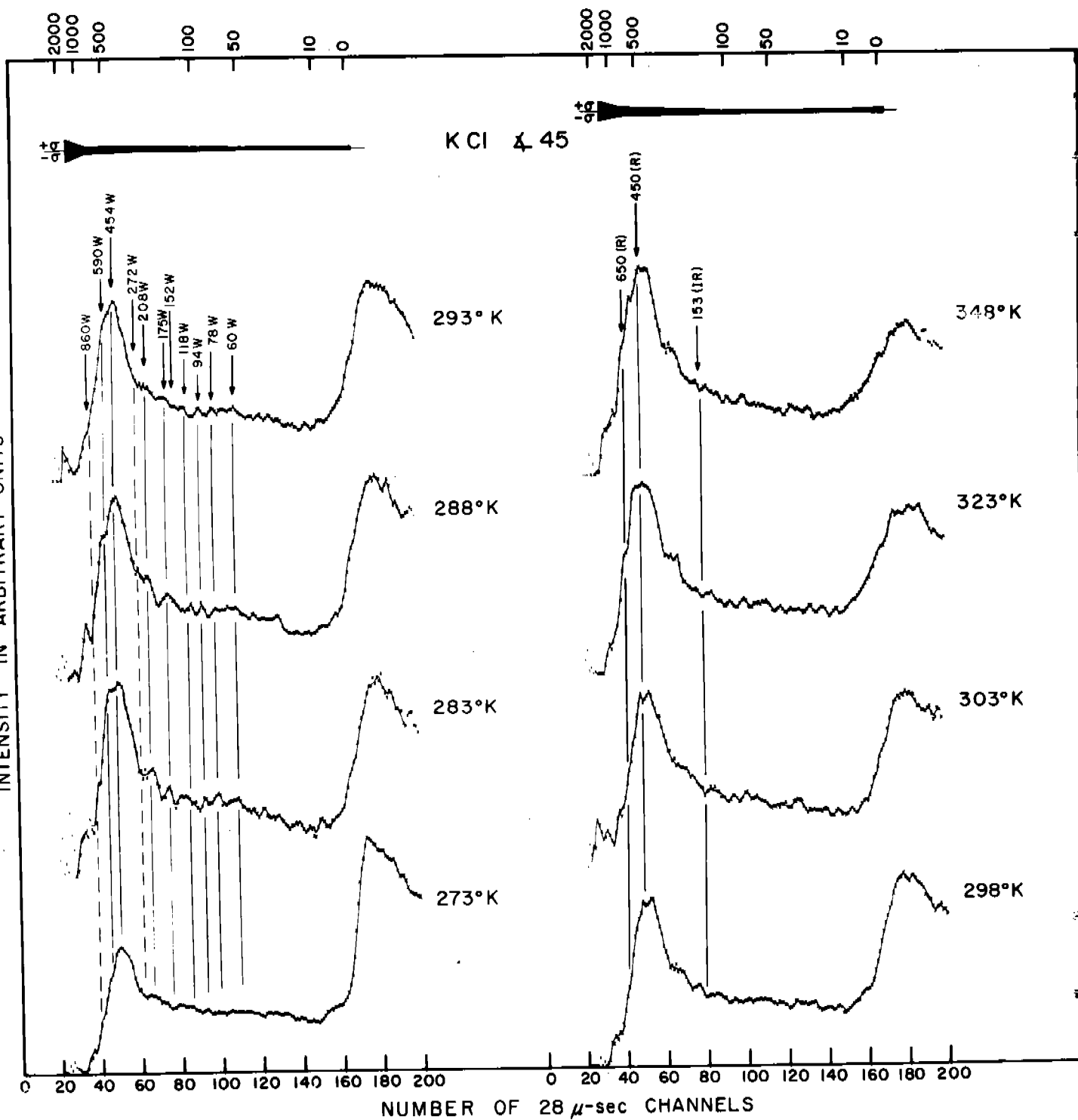and Williams[42], respectively.

NEUTRON ENERGY GAIN (cm⁻¹)

KCl ⊻ 45

INTENSITY IN ARBITRARY UNITS

NUMBER OF 28 μ-sec CHANNELS

FIGURE 12

The dependences of observed Γ vs. K^2 with concentration and temperature are shown for CsCl and KSCN solutions.
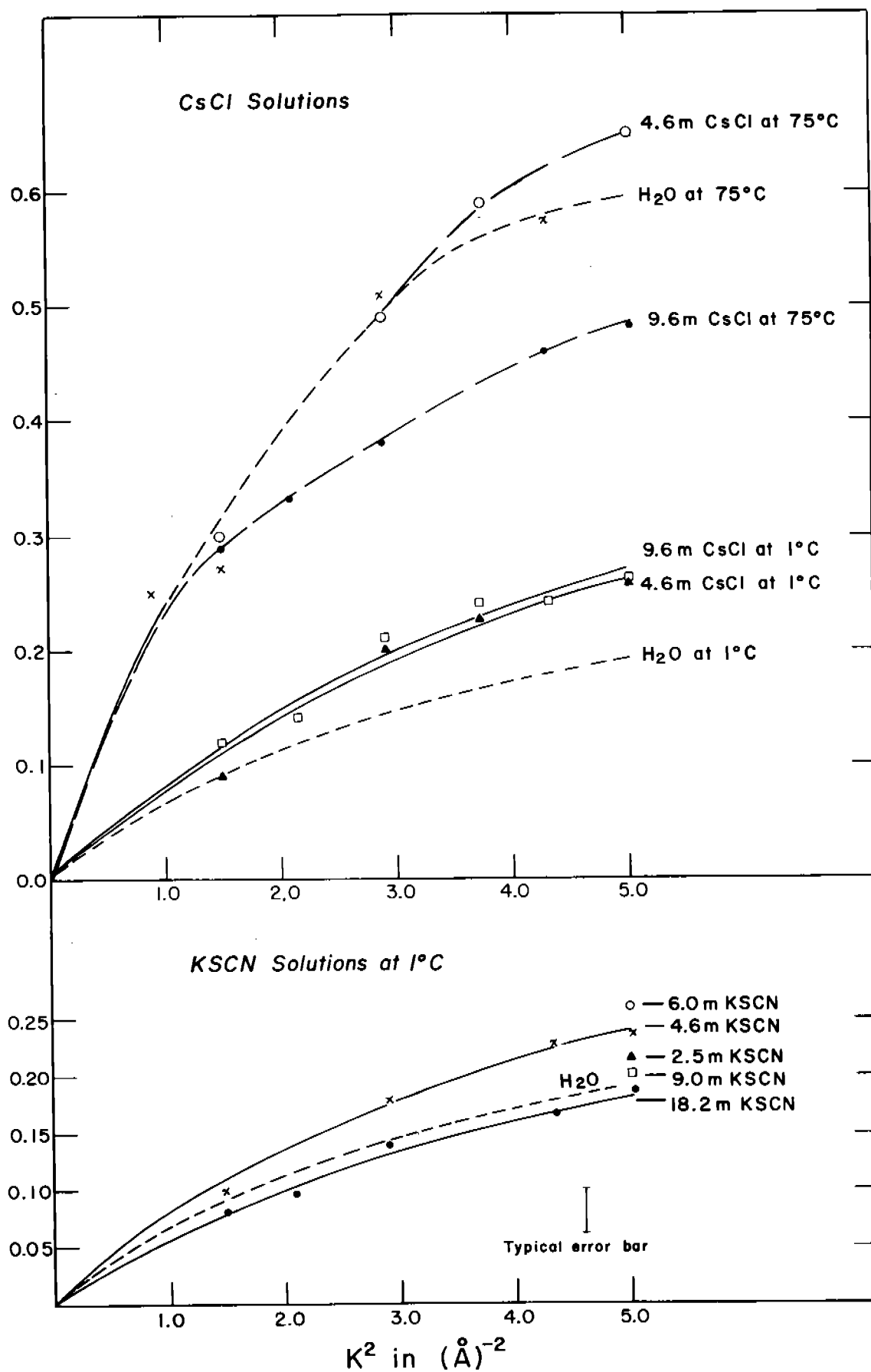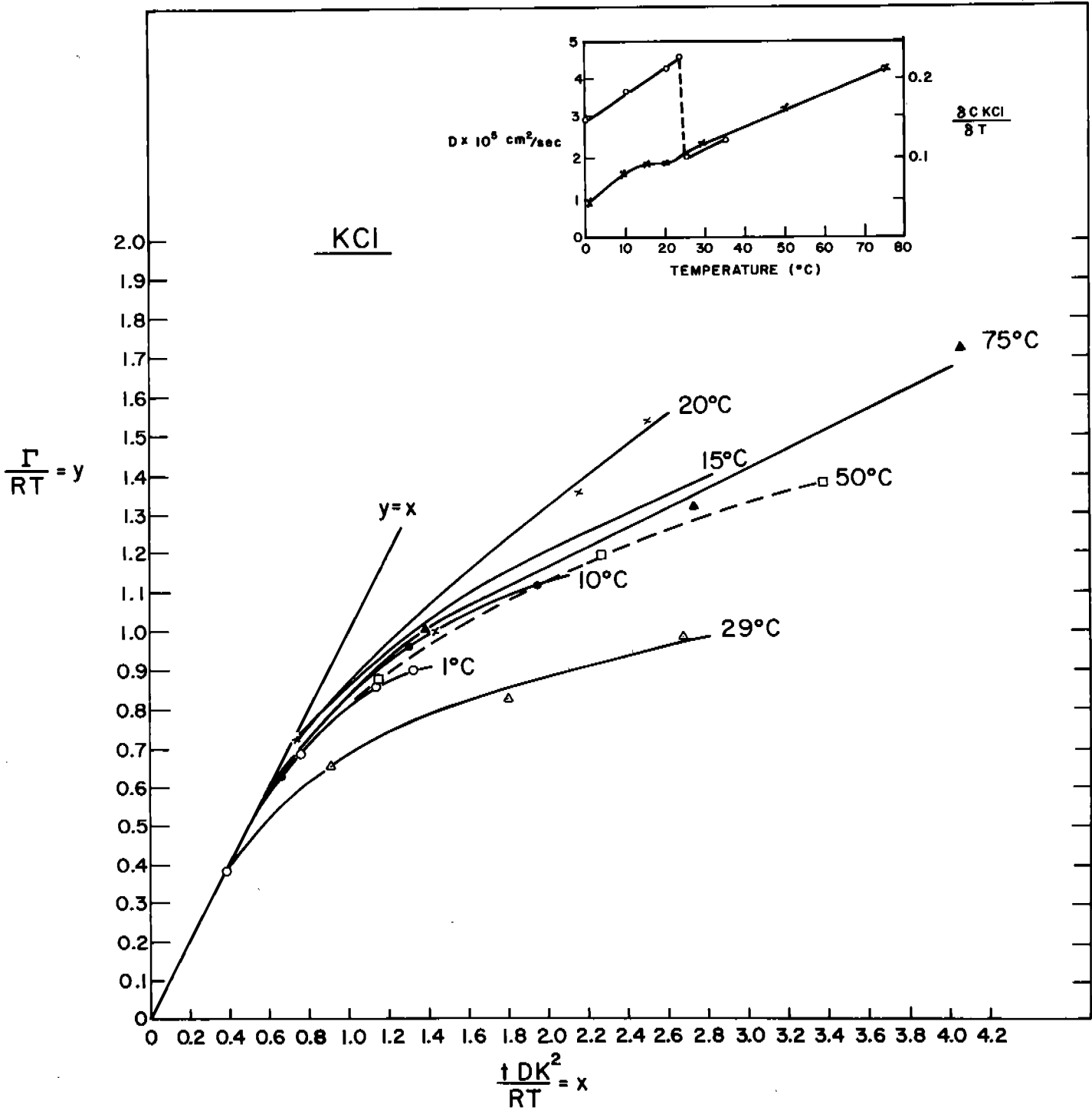
FIGURE 13

The observed temperature dependences of Γ/k_BT vs. $\hbar DK^2/k_BT$ are shown for 4.6 m KCl (3.2 m at 1°C) solution. In the inset the values of the self-diffusion coefficients obtained from the initial slopes of the Γ vs. K^2 curves are plotted versus temperature as X's. The temperature derivative of the solubility[22] is also plotted as a function of temperature (open circles).

REFERENCES

1. G.J. Safford, P.S. Leung, A.W. Naumann, and P.C. Schaffer, J. Chem. Phys. 50, 4444 (1969).

2. K.E. Larsson and U. Dahlborg, J. Nucl. Energy 16A/B, 81 (1962).

3. (a) G.J. Safford, P.S. Leung, P.C. Schaffer, Research and Development Progress Report No. 372, Office of Saline Water, U.S. Government Printing Off.,Washington DC (1968). (b) K.E. Larsson, in Thermal Neutron Scattering, P.A. Egelstaff, Ed. (Academic Press Inc., New York, 1965), p. 347.

4. T. Springer, Nuckleonik 3, 110 (1961). This paper constitutes one of the most complete reviews of the application of neutron scattering to the studies of vibrations and of diffusive motions of H_2O molecules in water and ice to be found in the literature. Pertinent theories and infrared and Raman measurements are also reviewed.

5. K.E. Larsson, Inelastic Scattering Neutrons, Proc. Symp. 4th Bombay, 1964, 2, 3 (1965).

6. I. Nakagawa and T. Shimanouchi, Spectrochim. 20, 429 (1964).

7. K.S. Singwi and A. Sjölander, Phys. Rev. 119, 863 (1960).

8. O. Ya Samoilov, Structure of Aqueous Electrolyte Solutions and the Hydration of Ions (Consultants Bureau Enterprises, Inc. New York, 1965).

9. H.S. Frank and W.Y. Wen, Discussions Faraday Soc. 24, 133 (1957).

10. V.I. Tickhomirov, J. Struct. Chem. $\underline{4}$, 479 (1963).

11. G.J. Safford and A.W. Naumann, J. Chem. Phys. $\underline{45}$, 3787 (1966).

12. Thermal Neutron Scattering, P. A. Egelstaff, Ed. (Academic Press Inc., New York, 1965).

13. G.J. Safford, P.C. Schaffer, P.S. Leung, G.F. Doebbler, G.W. Brady and E.F.X. Lyden, J. Chem. Phys. $\underline{50}$, 2140 (1969).

14. B.N. Brockhouse, Nuovo Cimento Suppl. $\underline{9}$, 45 (1958).

15. A.N. Goland and K. Otnes, Phys. Rev. $\underline{153}$, 184 (1967).

16. J.C. Hindman, J. Chem. Phys. $\underline{36}$, 1000 (1962).

17. D.E. Woessner, B.S. Snowden, Jr., and A.G. Ostroff, J. Chem. Phys. $\underline{49}$, 371 (1968).

18. L. Endom, H.G. Hertz, B. Thül, and M.D. Zeidler, Ber. Bunsenges. Physik. Chem. $\underline{71}$, 1008 (1967).

19. V.I. Ionov and R.K. Mazitov, Zhur. Strukt. Khimii $\underline{9}$, 895 (1968).

20. M. Eigen and E. Wicke, Z. Elektrochem. $\underline{55}$, 344 (1951).

21. G.W. Brady and J.T. Krause, J. Chem. Phys. $\underline{27}$, 304 (1957).

22. M.I. Schakhparanov, Zhur. Fiz. Khim. $\underline{27}$, 111 (1953).

23. V.I. Danilow and W.E. Neumark, Z. Physik. Sowjetunion $\underline{10}$, 673 (1936).

24. P.A. Egelstaff, Advan. Phys. $\underline{11}$, 203 (1962).

25. B.P. Fabricand, S.S. Goldberg, R. Leifer and S.G. Ungar, Mol. Phys. $\underline{7}$, 425 (1964).

26. I. Beck, Z. Phys. $\underline{40}$, 474 (1939).

27. G. Zundel and A. Murr, Z. Phys. Chem. $\underline{54}(1/2)$, 49 (1967).

28. J.B. Hasted and G.W. Roderick, J. Chem. Phys. $\underline{29}$, 17 (1958).

29. E. Glueckauf, Trans. Faraday Soc. $\underline{61}$, 914 (1965).

30. R.M. Lawrence and R.F. Kruh, J. Chem. Phys. 47, 4758 (1967).

31. R.G. Bryant, J. Phys. Chem. 73, 1153 (1969).

32. M. Kaminsky, Disc. Faraday Soc. 24, 171 (1957).

33. A.S. Solovkin, Zhur. Strukt. Khimii 9, 305 (1968).

34. G.A. Andreev, Proc. Acad. Sci. USSR, Phys. Chem. Sect. 145, 518 (1962).

35. H.S. Frank and M.W. Evans, J. Chem. Phys. 13, 507 (1945).

36. T.H. Cannon and R.E. Richards, Trans. Faraday Soc. 62, 1378 (1966).

37. R.E. Hester and W.E.L. Grossman, Spectro. Chim. Acta 23A, 1945 (1967).

38. Yu. P. Syrnikov, Zhur. Strukt. Khimii 7, 489 (1966).

39. G.W. Brady, J. Chem. Phys. 28, 464 (1958).

40. G.E. Walrafen, J. Chem. Phys. 44, 1546 (1966).

41. J.O. Burgman, J. Sciesinski and K. Sköld, Phys. Rev. 808, 170 (1968).

42. D.A. Draegert and D. Williams, J. Chem. Phys. 48, 401 (1968).

43. J.P. Mathieu and M. Lounsbery, Compt. rend. 229, 1315 (1949).